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(54) ELECTROCONDUCTIVE PASTE FOR METAL-PLATING SUBSTRATE

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain an electroconductive paste for metal-plating substrate which mainly comprises a specific electricconductive powder, a binder a curing agent and a solvent and is useful for preparing an inexpensive and solderable circuit board excellent in adhesion to the insulating substrate after metal plating and in resistances to hear and humidity.

SOLUTION: This electrocondutive paste mainly comprises (A) an electroconductive powder of silver particles of 1-20 μ m particle sizes prepared by three-dimensionally agglomerating primary silver particles with a primary particles sizes of 0.1-5 μ m, (B) a binder of a polyester prepared from the acid component containing 50-100mol% of an aromatic or alicyclic dicarboxylic acid and 0-50mol% of other dicarboxylic acids and the glycol component containing 60-100mol% of a 5-10C alkylene glycol and 0-40mol% of other glycols and 20-200mol%, based on the acid components, of ϵ -caprolactone having a glass transition temperature of -50 -20°C, a reduced viscosity of \geq 0.3dl/g, (C) a curing agent and (D) a

solvent. In addition, the weight ratios of A/(B+C) and B/C are set to 60/40-95/5 and 50/50-99/1, respectively.

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CLAIMS

[Claim(s)]

[Claim 1]Electric conduction powder (A).

Copolymerized polyester.

Are the above the conductive paste for metal plating grounds which it had, and electric conduction powder (A), Primary particles of silver with a particle diameter of 0.1-5 micrometers make a subject a secondary particle with a particle diameter of 1-20 micrometers formed by being connected in the shape of a three dimension, and it said copolymerized polyester, An acid component unit which consists of 0-50 mol of dicarboxylic acid % of 50-100 mol of dicarboxylic acid % and others chosen from among aromatic dicarboxylic acid and alicycle fellows dicarboxylic acid, A glycol component unit which a carbon number of a main chain becomes from 0-40 mol of glycol % of 60-100 mol of alkylene glycol % and others of 5-10, 20-200-mol% of epsilon-caprolactone unit is made into a constitutional unit to a total acid component unit, Glass transition point temperature is -50-20 **, and reduced viscosity is what is 0.3 or more dl/g, It is characterized by (B)/(C) being 50 / 50 - 99/1 (weight ratio) comparatively of a hardening agent [as opposed to / (A)/((B) + (C)) is 60/40-95/5 (weight ratio) comparatively, and / a binding material (B)] (C) of the total quantity of a binding material (B) and a hardening agent (C) to electric conduction powder (A).

[Claim 2]The conductive paste according to claim 1, wherein a hardening agent (C) is an isocyanate compound.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to conductive paste, in more detail, it is printed and hardened, forms a circuit on insulating base materials, such as a film, and relates to the conductive paste for metal plating grounds used in order to perform metal plating on this and to create a circuit.

[0002]

[Description of the Prior Art]Now, FPC which etched the copper-clad polyimide film (FCL) into the flexible printed circuit, and formed the circuit is used. Soldering is possible for this FPC and it is an outstanding material having still more advanced flexibility, reliability, and heat resistance. However, since the polyimide film which is a substrate is expensive and also many work processes including an etching process are required, FPC is dramatically expensive and development of a cheap circuit material replaced with FPC is demanded.

[0003]On the other hand, on the PET film, by low cost, the membrane circuit which printed conductive paste is lightweight, and is widely used by a keyboard, switch, etc. However, usually silver or carbon paste is used for conductive paste, and soldering is not made, but mounting of parts is difficult. Since it is quite high as compared with copper foil, circuit resistance is also inferior to an impedance characteristic, and there is a fault by which a use is limited to large **.

[0004]In order to solve **** between the above, by having printed and hardened conductive paste to the insulating base material, and also carrying out metal plating, it is cheap and the additive process which creates the circuit material which has about the same performance as FPC is examined. For example, although the additive process is indicated to JP,6-120643,A, JP,60-136394,A, JP,64-51691,A, etc., Each conductive paste currently used in these gazettes is commercial conductive paste for membranes as it is, conductive paste is not examined

enough but there is nothing satisfying. That is, although the adhesion over the substrate in the state where printed conductive paste given in the above to the insulating base material, and it hardened is enough, since the good adhesive strength to a substrate is not obtained but it is further inferior also to endurance, such as moisture resistance and heat resistance, when metal plating is carried out on this, it is hardly put in practical use.

[0005]The additive process which used ultraviolet-rays or electron beam hardening type conductive paste is examined by JP,61-224491,A and JP,57-15487,A. Since these things do not need hot heat treatment at the time of conductive paste hardening, although modification of substrates, such as a paper phenol board, can be prevented, the adhesive strength after metal plating is inferior, and is not put in practical use. In particular, to flexible substrates, such as a polyimide film and a PET film, remarkably, ***** can be inferior and cannot use it. Since heat resistance and moisture resistance are also inferior, these things are hardly put in practical use.

[0006]Conductive paste is indicated also to JP,59-206459,A. Although this thing is silver paste for membrane circuits which uses the usual shape of a flake or spherical silver dust, and polybutadiene system binder, Although the comparatively good characteristic is obtained in anticipated use (use which does not carry out metal plating), if metal plating is performed on this, good ** arrival intensity will not be obtained. Although the silver paste which uses copolymerized polyester resin as flake-like (shape of scaphocerite) silver dust and a binder is furthermore indicated by JP,1-159906,A, Although it has the adhesion, flexibility, and conductivity which were excellent in anticipated use also in this case, if it is used for the ground of metal plating, good adhesive strength will not be obtained.

[0007]

[Problem(s) to be Solved by the Invention]The purpose of this invention solves the problem of the above-mentioned conventional technology, and can improve substantially the adhesive property after metal plating to the organic film represented by various insulating base materials, especially PET, and there are environmental capabilities, such as heat resistance and moisture resistance, in providing the good conductive paste for metal plating grounds further. A cheap circuit material which can be soldered can be created with the conductive paste for metal plating grounds of this invention.

[0008]

[Means for Solving the Problem]Conductive paste which contains electric conduction powder which makes a silver granule child of specific structure a subject, and a specific copolymerized polyester binding material as a result of this invention persons' inquiring wholeheartedly, in order to solve such a problem, An adhesive property after plating to an organic film represented by insulating base material division PET was remarkably high, found out excelling also in heat resistance and moisture resistance further, and reached this invention.

[0009]Namely, conductive paste for metal plating grounds of this invention, Use it, when carrying out metal plating and forming a circuit, after printing this conductive paste to an insulating base material, and Electric conduction powder (A), In conductive paste used as the main ingredients, a binding material (B) which consists of copolymerized polyester, a hardening agent (C) which can react to a binding material (B), and a solvent (D) electric conduction powder (A), Primary particles of silver with a particle diameter of 0.1-5 micrometers make a subject a secondary particle with a particle diameter of 1-20 micrometers formed by being connected in the shape of a three dimension, and it said copolymerized polyester, An acid component unit which consists of 0-50 mol of dicarboxylic acid % of 50-100 mol of dicarboxylic acid % and others chosen from among aromatic dicarboxylic acid and alicycle fellows dicarboxylic acid, A glycol component unit which a carbon number of a main chain becomes from 0-40 mol of glycol % of 60-100 mol of alkylene glycol % and others of 5-10, 20-200-mol% of epsilon-caprolactone unit is made into a constitutional unit to a total acid component unit, glass transition point temperature is -50-20 **, and reduced viscosity is what is 0.3 or more dl/g, It is characterized by (B)/(C) being 50 / 50 - 99/1 (weight ratio) comparatively of a hardening agent [as opposed to / (A)/((B) + (C)) is 60/40-95/5 (weight ratio) comparatively, and / a binding material (B)] (C) of the total quantity of a binding material (B) and a hardening agent (C) to electric conduction powder (A). In the above, a mole ratio of a total acid component unit and a total glycol component unit is 1:1.

[0010]Hereafter, this invention is explained in detail.

[0011]Electric conduction powder (A) used for this invention makes a subject a secondary particle with a particle diameter of 1-20 micrometers formed when primary particles of silver with a particle diameter of 0.1-5 micrometers condensed in the shape of a three dimension, as shown in drawing 1 - 3. That is, drawing 1 - 3 are the electron microscope photographs of a silver granule child who forms a subject of electric conduction powder used by this invention, and, as for 1200 times and drawing 2, 3200 times and drawing 3 of drawing 1 are 8000 times as many photographs, respectively. Shape of this silver dust completely differs from shape of publicly known arborescence (the shape of a dendrite) looked at by electrolysis silver etc. which were indicated to above-mentioned JP,1-159906,A etc.

[0012]This silver granule child's desirable specific surface area is $1.3\text{-}2.2\text{m}^2/\text{g}$ preferably to $1.0\text{-}2.5\text{m}^2/\text{g}$ and a pan. An adhesive property after outstanding metal plating to a flexible organic film represented by an insulating base material, especially PET is acquired by using silver dust of this shape for a surprising thing. Although good specific resistance is obtained in publicly known flaky silver powder, adhesive strength after metal plating is not low practical, and in spherical silver powder, specific resistance becomes remarkably high and cannot use it. Paste viscosity becomes high and adhesive strength after metal plating of publicly known arborescence (shape of dendrite) silver dust mentioned above is also poor undesirably. Flaky

silver powder publicly known in the range which does not fall the characteristic as electric conduction powder (A) used for this invention, Although spherical silver powder, arborescence silver dust, graphite powder, carbon powder, nickel powder, copper powder, aluminum powder, indium powder, etc. may be used together, it is required for total conductive powder volume to use preferably secondary particles of silver of the above-mentioned specific shape as shown in drawing 1 - 3 70% of the weight or more 50% of the weight or more.

[0013]By a method of a statement, to JP,56-69309,A etc., such secondary particles of silver of specific shape oxidize under a specific condition, return silver nitrate, and are obtained.

[0014]the total quantity of a binding material (B) and a hardening agent (C) -- it is 60 / 40 - 95/5 (weight ratio) as (A)/((B) + (C)) comparatively, and is 70 / 30 - 85/15 preferably. [on this invention and as opposed to electric conduction powder (A) in loadings of electric conduction powder (A)] Conductivity whose loadings of (A) are good at less than 60/40 (weight ratio) is not obtained, but on the other hand, if 95/5 (weight ratio) is exceeded, an adhesive property after metal plating to an organic film will fall.

[0015]An acid component unit which consists of the dicarboxylic acid 50 - the 100-mol dicarboxylic acid 0 of % and others -, and 50-mol % as which a binding material (B) used for this invention is chosen from among aromatic dicarboxylic acid and alicycle fellows dicarboxylic acid, A glycol component unit which a carbon number of a main chain becomes from 0-40 mol of glycol % of 60-100 mol of alkylene glycol % and others of 5-10, To all the acid or a glycol component unit, by making 20-200-mol% of epsilon-caprolactone unit into a constitutional unit, glass transition point temperature is -50-20 **, and reduced viscosity consists of copolymerized polyester which is 0.3 or more dl/g. By using this binding material (B), it excels in an adhesive property after metal plating to various substrates, especially polyester film, and environmental capabilities, such as heat resistance and moisture resistance, serve as dramatically excellent conductive paste further.

[0016]a copolymerized polyester binding material (B) -- glass transition point temperature -it is -35--15 ** still more preferably, and 50-20 ** of reduced viscosity [-35-0 ** of / 0.3 or more dl/g of] are 0.5 - 1.5 dl/g preferably. An adhesive property after metal plating whose glass transition point temperature is good less than [-50 **] is not acquired, and environmental capabilities, such as moisture resistance, get worse. On the other hand, if 20 ** is exceeded, good breaking strength and the degree of breaking extension after hardening will not be obtained, and, for this reason, a good adhesive property after metal plating will not be acquired. By less than 0.3 dl/g, the good degree of breaking extension after hardening is not obtained for reduced viscosity, and an adhesive property after metal plating good for this reason is not acquired. Paste viscosity falls and it is not desirable.

[0017]An acid component unit which constitutes a copolymerized polyester binding material (B), 50-100 mol of dicarboxylic acid % chosen from among aromatic dicarboxylic acid and

alicyclic dicarboxylic acid -- desirable -- 0-50 mol % of dicarboxylic acid % of 70-100-mol % and others -- it consists of 0-30-mol % preferably. That is, dicarboxylic acid of others in here is arbitrary ingredients. Less than [50 mol %], aromatic dicarboxylic acid and/or alicyclic dicarboxylic acid become poor [environmental capabilities, such as heat resistance and moisture resistance,].

[0018]Here, as aromatic dicarboxylic acid, terephthalic acid, isophthalic acid, orthophthalic acid, 2, and 6-naphthalene dicarboxylic acid etc. are mentioned, for example. As alicyclic dicarboxylic acid, for example 1, 4-cyclohexanedicarboxylic acid, 1, 3-cyclohexanedicarboxylic acid, 1, 2-cyclohexanedicarboxylic acid, 4-methylhexahydrophthalic anhydride, 3-methylhexahydrophthalic anhydride, 2-methylhexahydrophthalic anhydride, dicarboxy hydrogenation bisphenol A, the dicarboxy hydrogenation bisphenol S, hydrogenation dimer acid, hydrogenation naphthalene dicarboxylic acid, tricyclodecane dicarboxylic acid, etc. are mentioned. Although the characteristic also with a good alicyclic dicarboxylic acid independent can be obtained, it is more preferred to use aromatic dicarboxylic acid independently or to use together with alicyclic dicarboxylic acid.

[0019]As other dicarboxylic acid, for example Succinic acid, glutaric acid, adipic acid, Aliphatic dicarboxylic acid, such as sebacic acid, dodecane dicarboxylic acid, and azelaic acid; SLB-12, ULB-20, SL-20, SB-20, ST-2, PML-6CM, Dibasic acid of the carbon numbers 12-28, such as IPU-22 (all are the products made from Okamura Oil Mill); Unsaturated dicarboxylic acid, such as dimer acid and boletic acid, etc. are mentioned. It is especially preferred from a point of environmental capabilities, such as adhesive strength after metal plating, heat resistance, and moisture resistance, to use with a carbon numbers of nine or more of sebacic acid, dodecane dione acid, etc. aliphatic dicarboxylic acid and with a carbon numbers of 12 or more dibasic acid at less than 30 mol % among other dicarboxylic acid.

[0020]Acid anhydrides, such as trimellitic anhydride and phthalic anhydride, may be back-added, and acid value may be given. Sulfonic acid metal salt content dicarboxylic acid, such as 5-sulfoisophtharate sodium salt, may be used together in the range which does not spoil the contents of the invention to unsaturated dicarboxylic acid, such as polyvalent carboxylic acid, such as trimellitic anhydride and pyromellitic dianhydride, and boletic acid, and a pan.

[0021]a glycol component unit which constitutes a copolymerized polyester binding material (B) -- a carbon number of a main chain -- the alkylene glycol 60 of 5-10 - 100-mol % -- desirable -- the glycol 0 of 80 - 100-mol % and others - 40-mol % -- it consists of 0 - 20-mol % preferably. That is, glycols of others in here are arbitrary ingredients.

[0022]Here as alkylene glycol of the carbon numbers 5-10 of a main chain, For example, 1,5-pentanediol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, 2-methyl-1,5-pentanediol, 1,9-nonanediol, 1,10-Decanediol, etc. are mentioned, and it is independent or is used combining two or more kinds. such long-chain glycols -- more than 60 mol % -- by using it, an adhesive

property and heat resistance after good metal plating are obtained, and moisture resistance improves remarkably to a still more surprising thing.

[0023]As other glycols, for example Ethylene glycol, neopentyl glycol, Propylene glycol, 1,3-propanediol, 2,2-diethyl- 1,3-propanediol, With a carbon number of less than five of main chains, such as 2-butyl-2-ethyl-1,3-propanediol and 1,4-butanediol, alkylene glycol; 1, 4-cyclohexane dimethanol, Alicycle fellows glycols, such as 1,3-cyclohexane dimethanol, 1,2-cyclohexane dimethanol, and TCD glycol; *****, such as dimer diol. It is [among these] preferred to use alicycle fellows glycols, such as neopentyl glycol and 1,4-cyclohexanediol, at less than 20 mol % from a damp-proof field. Multivalent polyols, such as trimethylolethane, trimethylolpropane, glycerin, pentaerythritol, and polyglycerin, may be used together in the range which does not spoil the contents of the invention.

[0024]A copolymerized polyester binding material (B) is what makes a constitutional unit preferably 50 - 150-mol% of epsilon-caprolactone unit 20 - 200-mol% to said all the acid or a glycol component unit again. By carrying out copolymerization of the epsilon-caprolactone, adhesive strength after dramatically outstanding metal plating is obtained, and it is obtained in still better heat resistance and moisture resistance. An adhesive property in which epsilon-caprolactone unit is good less than [20 mol %] is not acquired, but on the other hand, if 200-mol % is exceeded, environmental capabilities, such as heat resistance and moistness, will get worse.

[0025]Although a copolymerized polyester binding material (B) is constituted as mentioned above, it can obtain it by the ability to carry out the polycondensation of this under decompression by a publicly known method. epsilon-caprolactone is taught, after making dicarboxylic acid and glycol react and Ester-izing about epsilon-caprolactone, Under decompression, a polycondensation can be carried out, or it can also be used, being able to carry out the bottom of ordinary pressure after a polymerization under decompression of copolymerized polyester, being able to back add epsilon-caprolactone at 180-230 °C (ring opening addition), and blocking.

[0026]In this invention, it is a range which does not spoil the contents of the invention to the above-mentioned copolymerized polyester binding material (B), and an epoxy resin or phenol resin may be blended. Loadings in this case are usually about 5 to 20 % of the weight to a copolymerized polyester binding material (B). Adhesive strength after metal plating increases by blending a proper quantity of these resin.

[0027]A hardening agent (C) which can react to a binding material (B) used by this invention has points, such as an adhesive property, flexibility, and hardenability, to especially a preferred isocyanate compound, although the kind is not limited. As for these isocyanate compounds, it is preferred from a point of storage stability to use it, Plock-izing. As hardening agents other than an isocyanate compound, it is mentioned in publicly known compounds, such as amino

resin, such as methylation melamine, butyl-ized melamine, benzoguanamine, and urea resin, an acid anhydride, imidazole derivatives, an epoxy resin, and phenol resin.

[0028]As an isocyanate compound, there may be diisocyanate of aromatic series and aliphatic series and polyisocyanate more than trivalent, and any of a low molecular weight compound and a high molecular compound may be sufficient. For example, tetramethylene di-isocyanate, hexamethylene di-isocyanate, Toluene diisocyanate, diphenylmethane diisocyanate, hydrogenation diphenylmethane diisocyanate, Xylylene diisocyanate, hydrogenation xylylene diisocyanate, isophorone diisocyanate or a trimer of these isocyanate compounds, and an excessive amount of these isocyanate compounds, For example, ethylene glycol, propylene glycol, trimethylolpropane, Glycerin, sorbitol, ethylenediamine, monoethanolamine, An end isocyanate group content compound etc. which are produced by making react to a polymers active hydrogen compound of low molecule active hydrogen compounds, such as diethanolamine and triethanolamine, or various polyester polyol, polyether polyol, and polyamide, etc. are mentioned.

[0029]As a block isocyanate-ized agent, for example Phenol, a thiophenol, Methylthio phenol, an ethylthiophenol, cresol, a xylenol, Phenols, such as resorcinol, a nitrophenol, and chlorophenol; Acetoxime, Oxime, such as methylethyl ketoxime and cyclohexanone oxime; Methanol, Alcohols, such as ethanol, propanol, and butanol; Ethylene chlorohydrine, Halogenation alcohols, such as 1 and 3-dichloro-2-propanol; Tertiary alcohol, such as t-butanol and t-pentanol; Lactam, such as epsilon caprolactam, delta-valerolactam, gamma-butyrolactam, and beta-PUROPIRO lactam, is mentioned. Active methylene compounds, such as aromatic amine, imide, an acetylacetone, acetoacetic ester, and malonic acid ethyl ester, mercaptans, imine, imidazole derivatives, urea, diaryl compounds, sodium bisulfite, etc. are mentioned besides **. Oxime, imidazole derivatives, and especially amines are [among these] more preferred than hardenability.

[0030]In these hardening agents, a publicly known catalyst or an accelerator selected according to the kind can also be used together.

[0031]In this invention, rate [of a hardening agent (C)] (B)/(C) to a binding material (B) and a (weight ratio) are 50 / 50 - 99/1. (B) If / (C) separates from this range, flexibility and an adhesive property after metal plating will become poor. (B)/(C) is 70 / 30 - 85/15 preferably.

[0032]The kind is not limited and, as for a solvent (D) used by this invention, solvents, such as an ester system, a ketone system, an ether ester system, a chlorine system, an alcohol system, an ether system, and a hydrocarbon system, are mentioned, for example. When screen-stenciling, retarder thinner, such as ethylcarbitol acetate, butyl-cellosolve acetate, isophorone, and cyclohexanone, is [among these] preferred. Generally the amount of solvent (D) used is about 45-60 weight sections to conductive paste 100 weight section.

[0033]Various additive agents other than electric conduction powder (A), a binding material

(B), a hardening agent (C), and a solvent (D), such as a defoaming agent, a leveling agent, and a dispersing agent, can be blended with conductive paste of this invention if needed.

[0034] It is preferred that the degree of breaking extension after [a field of adhesive strength after metal plating to] hardening is high, the degree of breaking extension is preferred, and conductive paste of this invention is not less than 80% still more preferably not less than 20%. An adhesive property after metal plating with the degree of breaking extension good at less than 20% is not acquired.

[0035]

[Example] Next, this invention is more concretely explained using an example. A part and a certain thing only show a weight section among an example. Each parameter followed the following methods.

[0036] 1. With the viscosity of 25**1 **, it measured at a 3-degree corn and 5 rpm with E type rotation viscometer.

[0037] 2. :thixotropy degree = viscosity (2.5 rpm) / viscosity which measured viscosity at 3-degree corn and 2.5 rpm/10rpm with E type rotation viscometer with degree of thixotropy of 25**1 **, and computed degree of thixotropy with following formula (10 rpm)

[0038] 3. Reduced viscosity (dl/g)

Sample resins were dissolved in phenol / tetrachloroethane (60/40 weight ratio) mixed solvent by the concentration of 0.400g/100 ml, and it measured at 30 ** using the Ostwald viscosity meter.

[0039] 4. The number average molecular weight of polystyrene conversion was measured by molecular weight GPC.

[0040] 5. Glass transition point temperature (Tg)

It measured with 20 ** the heating rate for /using the differential scanning calorimeter (DSC). The sample put 5 mg of samples into the aluminum presser-foot lid shaped container, and carried out crimp.

[0041] 6. 0.2 g of acid value samples were weighed precisely, and it dissolved in 20 ml of chloroform. Subsequently, it titrated and asked with the potassium hydrate (ethanol solution) of 0.01N. The phenolphthalein solution was used for the indicator.

[0042] 7. The specific resistance of the conductive paste which carried out heat cure for 30 minutes was measured using 4 deep-needle measure resistance machine by 150 ** of specific resistance.

[0043] 8. Conductive paste was used for the annealing treatment finishing PET film of 75 micrometers of adhesive strength after metal plating, the line of 1-mm width was screen-stenciled, and heat cure was carried out for 30 minutes at 150 **. Subsequently, after it washes by NaOH 5% and 50-degree Baume sulfuric acid performs surface activity-ization, What performed copper plating so that copper thickness might be set to 30-35 micrometers by

3 A/dm² was made into the test piece using the copper sulfate system plating bath (it consists of 200 g/l of copper sulfate, 50 g/l of sulfuric acid, chloride-ion 50 mg/l, and a brightening agent). The back up plate was stuck on the test piece rear face with the double-sided tape, and a 90-degree friction test was done by 50 mm/min with the tension tester.

[0044]9. Breaking extension degree conductive paste was applied to the Teflon sheet by the applicator, 150 °C/after carrying out heat cure for 30 minutes, the coat was exfoliated, the tension tester pulled this by 50 mm/min, and the degree of breaking extension was measured. It measured by sample 1 cm in width, the sample length of 5 cm, and 30-40 micrometers of thickness.

[0045]10. After heat-treating the test piece created by heat-resistant above-mentioned 8. in hot wind oven at 85 °C for 1000 hours, the friction test was done and the retention of peel strength estimated.

[0046]11. The test piece created by damp-proof above-mentioned 8. was performed after 500-hour neglect, the friction test was done under 85 °C and the conditions of 85% of relative humidity, and the retention of peel strength estimated.

[0047]12. The silver dust of a mean-particle-diameter small quantity was taken to a 100-ml tall beaker, about 60 ml of isopropyl alcohol was put in, and the ultrasonic homogenizer distributed for 1 minute. This was measured with the grading analysis plan (made by a micro track company) by light scattering measurement, and particle diameter was made into mean particle diameter 50%.

[0048]13. The specific surface area silver dust 1-2g was taken to the sample cell, it pretreated on the conditions for 60 °C/5 minutes, and 10 °C/2 minutes, and the whole surface product was measured with the specific surface area automatic measuring instrument (the Micromeritics make, one BET adsorption method low-temperature N₂ gas adsorption method). The specific surface area per g was computed by having measured after-measurement sample weight and having divided the whole surface product by sample weight.

[0049][Synthetic example 1 (polyester resin I)] in the 4 mouth flask possessing a GUBIRYU rectifying tower. 58 copies of dimethylterephthalic acid, 136 copies of dimethylisophthalic acid, 33 copies of neopentyl glycol, 186 copies of 1,5-pentanediol, and 0.068 copy of tetrabutyl titanate were taught, and SL exchange was performed at 180 °C for 3 hours. Next, it decompressed gradually to 1 or less mmHg, and polymerized at 240 °C for 1 hour. Subsequently, it cooled at 200 °C under a nitrogen atmosphere, 114 copies of epsilon-caprolactones were taught, and it heated to 230 °C gradually over 1 hour. The presentation of the obtained copolymerized polyester is terephthalic acid / isophthalic acid / neopentyl glycol / 1,5-pentanediol / epsilon-caprolactone =30/70/14/86/100 (mole ratio).

They were reduced viscosity 0.70 dl/g, the number average molecular weight 24000, acid value 0.7 mgKOH/g, and Tg=-28 °C.

[0050][Synthetic examples 2-4] (polyester resin II-IV) By the same operation as the synthetic example 1, polyester resin II-IV was compounded from the desired monomer raw material, respectively. The presentation of the obtained copolymerized polyester, reduced viscosity, a number average molecular weight, acid value, and Tg are shown in Table 1.

[0051][Examples 1-2 of comparison composition] (comparison polyester resin V-VI) By the same operation as the synthetic example 1, the comparison polyester resin V-VI was compounded from the desired monomer raw material, respectively. The presentation of the obtained copolymerized polyester, reduced viscosity, a number average molecular weight, acid value, and Tg are shown in Table 2.

[0052][Example 3 of comparison composition] (comparison polyester resin VII) in the 4 mouth flask possessing a GUBIRYU rectifying tower. 101 copies of dimethylterephthalic acid, 35 copies of dimethylisophthalic acid, 93 copies of ethylene glycol, 73 copies of neopentyl glycol, and 0.068 copy of tetra PUCHIRU titanate were taught, and SL exchange was performed at 180 ** for 3 hours. Subsequently, 61 copies of sebacic acid was prepared and the esterification reaction was performed further. Next, it decompressed gradually to 1 or less mmHg, and polymerized at 240 ** for 1 hour. The presentation of the obtained copolymerized polyester is terephthalic acid / isophthalic acid / sebacic acid / ethylene glycol / neopentyl glycol =52/18/30/55/45 (mole ratio).

Reduced viscosity 0.64 dl/g, the number average molecular weight 22000, acid value 1.5 mgKOH/g, Tg = it was 7 **.

[0053][Examples 4-5 of comparison composition] (comparison polyester resin VIII-IX) By the same operation as the example 3 of comparison composition, comparison Voli ester resin VIII-IX was compounded from the desired monomer raw material, respectively. The presentation of the obtained copolymerized polyester, reduced viscosity, a number average molecular weight, acid value, and Tg are shown in Table 2.

[0054][Example 6 of comparison composition] (comparison polyurethane resin X) in a 4 mouth flask. Aliphatic series system polyesterdiol OD-X-688 (product made from Dainippon Ink Industry) 100 copy, Six copies of neopentyl glycol as a chain elongation agent, two copies of 1,6-hexanediol, 157 copies of ethylcarbitol acetate and 52 copies of butyl-cellosolve acetate are taught, It heated at 60 ** under the nitrogen air current, 31 copies of diphenylmethane diisocyanate was taught further, and it heated to 80 ** gently, and it reacted for 5 hours until the unreacted isocyanate was no longer detected. The obtained polyurethane resin was reduced viscosity 1.10 dl/g, the number average molecular weight 38000, and Tg=-32 **.

[0055][Silver dust preparation]

(Preparation of the silver dust A-1) 275 copies of silver nitrate aqueous solutions of 37% of

concentration and 220 copies of sodium hydroxide solution of 18% of concentration were made to react under churning at 40-50 **, and 70 copies of distilled water was added after ending reaction. Subsequently, 60 copies of formalin aqueous solution of 23% of concentration was added to this, and it was made to react at 30-40 **. pH after ending reaction was 8. After filtering the obtained silver dust and repeating rinsing and drying, it filtered, after methanol replaced and reduced pressure drying was carried out at 80 ** for 24 hours. The obtained silver dust has the shape shown in drawing 1 - 3, and the mean particle diameter of primary particles is 0.5 micrometer from a scanning electron microscope photograph. When the mean particle diameter of secondary particles was measured with light scattering measurement, it was 11-micrometer and specific surface area $1.62\text{m}^2/\text{g}$.

[0056](Preparation of the silver dust A-2) Commercial flaky silver powder (made by Fukuda Metal Foil & Powder) was used as it was. The mean particle diameter by light scattering measurement was 4.5 micrometers, and specific surface area was $0.70\text{m}^2/\text{g}$.

[0057](Preparation of the silver dust A-3) Commercial flaky silver powder (made by Fukuda Metal Foil & Powder) was used as it was. The 4.5-micrometer specific surface area of the mean particle diameter by light scattering measurement was $0.65\text{m}^2/\text{g}$.

[0058][Example 1] A-1:77.0 copy of silver dust, and the polyester resin I:17.3 solid part dissolved using butyl Cellosolve acetate as a solvent (D), A block isocyanate compound C-1 (hexamethylene di-isocyanate, butanooxime block body [of isocyanurate adduct], 80% of solid content):5.7 solid part, Polyamide-system dispersing agent: After blending 0.2 solid part and carrying out a premix enough, it let it pass 3 times, the three chilled roll kneading machine distributed, and silver paste was obtained. The obtained silver paste is viscosity 34.1 (pa-s), the degree 1.47 of thixotropy, specific resistance 9.0×10^{-5} omega-cm, and 180% of the degree of breaking extension.

The adhesive strength after copper plating was good at 1600 g/cm.

After giving copper plating, the adhesive strength retention after doing 500 time-environment examinations at 85 ** with 1000 hours and 85 **, and 85% of relative humidity is 82% and 95%, respectively.

It had a very good environmental capability.

The combination presentation of silver paste and the result of each property value are shown in Table 3.

[0059][Examples 2-5] The silver paste of the combination presentation as shown in Table 3 was created, respectively, and the same operation as Example 1 estimated it Example 1 similarly. A result is shown in Table 3.

[0060][Comparative examples 1-11] The silver paste of the combination presentation as shown

in Tables 4-5 was created, respectively, and the same operation as Example 1 estimated it Example 1 similarly. A result is shown in Tables 4-5.

[0061]

[Table 1]

ポリエステル樹脂		合成例 1 I	合成例 2 II	合成例 3 III	合成例 4 IV
組成・モル %	テレフタル酸	30	30	40	
	イソフタル酸	70	60	40	
	1,4-シクロヘキサンジカルボン酸			20	50
	1,2-シクロヘキサンジカルボン酸				50
	セバシン酸		10		
	1,5-ペンタンジオール	86			
	1,6-ヘキサンジオール		100	84	60
	ネオペンチルグリコール	14		16	40
	ε-カプロラクトン	100	100	50	40
	ガラス転移点温度 (°C)	-28	-40	-18	-39
還元粘度 (dl/g)		0.70	0.82	0.65	0.71
数平均分子量		24000	28000	21000	24000
酸価 (mg KOH/g)		0.7	1.0	0.8	1.0

[0062]

[Table 2]

比較ポリエステル樹脂		比較 合成例 1 V	比較 合成例 2 VI	比較 合成例 3 VII	比較 合成例 4 VIII	比較 合成例 5 IX
組成・モル %	テレフタル酸	20	30	52	30	45
	イソフタル酸	20	70	18	70	45
	アジピン酸	60				
	セバシン酸			30		10
	1,5-ペンタンジオール	85			85	
	ネオペンチルグリコール	15	38	45	15	45
	エチレングリコール		62	55		55
	ε-カプロラクトン	50	145	—	—	—
	ガラス転移点温度 (°C)	-45	-20	7	4	43
	還元粘度 (dl/g)	0.82	0.70	0.64	0.55	0.82
数平均分子量		25000	24000	22000	18000	25000
酸価 (mg KOH/g)		1.5	1.0	1.1	0.8	1.0

[0063]

[Table 3]

		実施例1	実施例2	実施例3	実施例4	実施例5
配 合	導電粉 (A) 重量部	A-1 77	A-1/A-2 46/31	A-1 77	A-1 72	A-1 82
	結合剤 (B) 固形部	ポリエス テル (I) 17.3	ポリエス テル (I) 17.3	ポリエス テル (II) 17.3	ポリエス テル (III) 21.0	ポリエス テル (IV) 13.5
	硬化剤 (C) 固形部	C-1 5.7	C-1 5.7	C-1 5.7	C-1 7.0	C-1 4.5
	分散剤 固形部	0.2	0.2	0.2	0.2	0.2
(A)/((B)+(C))		77/23	77/23	77/23	72/28	82/18
(B)/(C)		75/25	75/25	75/25	75/25	75/25
(B)のTg (°C)		-28	-28	-40	-18	-39
(B)の還元粘度 (dl/g)		0.70	0.70	0.82	0.65	0.71
塗 膜 物 性	破断伸度 (%)	180	180	280	220	165
	接着力 (g/cm)	1600	1250	1700	1700	1200
	比抵抗 ($\times 10^{-5} \Omega \cdot \text{cm}$)	9.0	5.4	10.0	55.0	7.2
	耐熱性 (%)	82	99	84	81	87
	耐湿性 (%)	95	95	98	96	97

[0064]

[Table 4]

		比較例1	比較例2	比較例3	比較例4	比較例5
配合	導電粉 (A) 重量部	A-2 89	A-3 77	A-2 89	A-1 77	A-1 77
	結合剤 (B) 固形部	ポリエス テル (I) 11.0	ポリエス テル (II) 17.3	ポリエス テル (VI) 9.4	ポリエス テル (V) 17.3	ポリエス テル (VI) 17.3
	硬化剤 (C) 固形部	C-1 2.8	C-1 5.7	C-2* 1.6	C-1 5.7	C-1 5.7
	分散剤 固形部	0.2	0.2	0.2	0.2	0.2
(A)/((B)+(C))		89/11	77/23	89/11	77/23	77/23
(B)/(C)		75/25	75/25	85/15	75/25	75/25
(B) の T _g (°C)		-28	-40	7	-45	-20
(B) の還元粘度 (dl/g)		0.70	0.82	0.64	0.82	0.70
塗膜物性	破断伸度 (%)	28	195	5	280	190
	接着力 (g/cm)	300	400	250	700	1050
	比抵抗 ($\times 10^{-5} \Omega \cdot \text{cm}$)	7.5	15.5	7.5	9.0	9.2
	耐熱性 (%)	98	97	75	32	35
耐湿性 (%)		95	95	35	10	25

* C-2 : ブロックイソシアネート化合物

(ヘキサメチレンジイソシアネート、

ビウレット3量体のメチルエチルケトオキシムブロック体)

[0065]

[Table 5]

		比較例6	比較例7	比較例8	比較例9	比較例10	比較例11
配合	導電粉 (A) 重量部	A-1 77	A-1 77	A-1 77	A-1 77	A-1 77	A-3 80
	結合剤 (B) 固形部	ポリエス テル (Ⅳ) 17.3	ポリエス テル (Ⅴ) 17.3	ポリウレ タン (X) 17.3	ポリエス テル (Ⅰ) 23.0	ポリエス テル (Ⅰ) 10.4	ポリブタジ エン*1 10
	硬化剤 (C) 固形部	C-1 5.7	C-1 5.7	C-1 5.7	— —	C-1 12.6	C-3*2 10
	分散剤 固形部	0.2	0.2	0.2	0.2	0.2	0.2
(A)/[(B)+(C)]		77/23	77/23	77/23	77/23	77/23	80/20
(B)/(C)		75/25	75/25	75/25	100/0	45/55	50/50
(B)のT _g (°C)		4	43	-32	-28	-28	—
(B)の還元粘度 (dl/g)		0.55	0.82	1.10	0.70	0.70	—
物性	破断伸度 (%)	10	3	180	65	25	45
	接着力 (g/cm)	150	175	1200	250	170	120
	比抵抗 ($\times 10^{-5} \Omega \cdot \text{cm}$)	10.0	10.0	9.5	9.5	10.0	55.0
	耐熱性 (%)	42	55	32	0	55	15
	耐湿性 (%)	98	45	15	0	80	10

*1) ポリブタジエン: R-45HT 末端水酸基ポリブタジエン (出光石油化学(株)製)

*2) C-3: ユーロックQ-9062

ポリブタジエン系フェノールブロック化イソシアネートプレポリマー
(出光石油化学(株)製)

[0066] Each silver paste of Examples 1-5 does not have a problem in specific resistance and the degree of breaking extension, the adhesive strength after copper plating is also better than Table 3, and it is still clearer this adhesive strength's for high retention to be shown after a heat resistance test and a humidity test, and to have a very good environmental capability.

[0067] On the other hand, each silver paste of the comparative examples 1-3, and 11 in which the silver dust A-1 is not used is inferior to Tables 4-5 in the adhesive strength after copper plating. Although the silver dust A-1 is used, each silver paste of the comparative examples 4-8 in which comparison polyester resin or comparison polyurethane resin is used as a binding material is remarkably inferior to heat resistance and moisture resistance. The adhesive strength after copper plating is also remarkably inferior in especially the silver paste of the comparative examples 4, 6, and 7. Since the hardening agent is not blended, the silver paste of the comparative example 9 is remarkably inferior to the adhesive strength after copper plating, heat resistance, and moisture resistance. Since the silver paste of the comparative example 10 has too many loadings of a hardening agent, it is remarkably inferior to the adhesive strength after copper plating.

[0068]

[Effect of the Invention] Since the conductive paste of this invention is constituted as mentioned

above, it is excellent in the adhesive property after metal plating to the organic film represented by various insulating base materials, especially PET, and its environmental capabilities, such as heat resistance and moisture resistance, are also dramatically good. Therefore, a cheap circuit material which can be soldered can be created with the conductive paste for metal plating grounds of this invention.

[Translation done.]